



## *Ab initio* Study of Alkyl-oxonium Cations $C_nH_{2n+1}OH_2^+$ , $n=1,2,3,4$

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**Abstract:** Within the framework of the itinerant radical model, the solvated electron in liquid alcohols is understood as an itinerant alkyl-oxonium  $ROH_2^{\cdot}$  radical. As a first step in the investigation of those radicals, this study deals with the optimization of related  $ROH_2^+$  alkyl-oxonium cations:  $C_nH_{2n+1}OH_2^+$ ,  $n=1,2,3,4$ . The structures were optimized at the MP2/6-31G\*\*++ level with the help of the GAMESS *ab initio* package. Optimized structures are reported for the following cations: MethylOxonium, EthylOxonium, 1-PropylOxonium, 2-PropylOxonium, 1-ButylOxonium, 2-ButylOxonium, IsoButylOxonium, and TertButylOxonium. Optimized geometries are displayed with the help of the ChemApp Java applet. Vibrational frequencies and ZPEs have been computed, and visual depictions of expected experimental IR spectra have been simulated with the help of Lorentzian functions.

**Keywords:** Alcohols, Oxonium cations, AlkylOxonium, MethylOxonium, EthylOxonium, PropylOxonium, PropylOxonium, ButylOxonium, *Ab initio*, GAMESS, CaChe, SMILES, CORINA, Itinerant Radical model, Solvated Electron, Radiation Chemistry, ChemApp, Java Applet.

### Introduction

According to the itinerant radical model [1],[2],[3], the entity that is currently called a hydrated electron or  $(e^-)_{aq}$  should be understood instead as the mobile  $H_3O^{\cdot}$  protic defect or itinerant hydronium radical. In a way similar to the F-center, also a neutral defect, the hydronium radical neutral defect moves under the influence of an electric field in the same direction as a negatively charged classical species.

Similarly, in alcohols, the solvated electron ( $e^-$ )<sub>solv</sub> should be understood as the itinerant alkyl-oxonium ROH<sub>2</sub><sup>·</sup> radical. This conception would help to understand why the absorption spectrum of the solvated electron ( $e^-$ )<sub>solv</sub> appears to depend on **chemical** properties, instead of **physical** properties such as the dielectric constant as predicted by the cavity model. Furthermore, Gordon Freeman and co-workers [4] discovered that the mobility of ( $e^-$ )<sub>solv</sub> is closely related to the mobility of ROH<sup>·</sup> in various alcohols, a fact which is very hard to understand within the framework of the cavity model. Within the itinerant radical model, on the contrary, it is expected that mobilities of ROH<sup>·</sup> and ROH<sub>2</sub><sup>·</sup> are related since both mobility mechanisms involve motion of itinerant protic defects.

So far to our knowledge, the structures and dynamics of positive protic defects ie ROH<sub>2</sub><sup>+</sup> in liquid alcohols have been theoretically studied only in liquid methanol by Mark Tuckerman and coworkers [5].

With the help of *ab initio* methods, it is not currently feasible to compute the absorption spectra of solvated alkyl-oxonium radicals. However we believe that the most important factor, that influences the absorption spectrum of various ROH<sub>2</sub><sup>·</sup> radical, is their respective intramolecular structures. Therefore, our ultimate goal is to compute the absorption spectra of a significant number of isolated alkyl-oxonium radicals. Then, we expect that computed isolated alkyl-oxonium radical respective spectral shifts should match with observed respective spectral shifts between "solvated electrons" in various alcohols.

As a first step towards determining of the absorption spectra of isolated ROH<sup>·</sup> in various alcohols in order to check the prediction of the itinerant radical model with experimental spectra, we have focused this study in determining the optimized geometries of the isolated ROH<sub>2</sub><sup>+</sup> alkyl-oxonium cations: C<sub>n</sub>H<sub>2n+1</sub>OH<sub>2</sub><sup>+</sup>, n=1,2,3,4.

Molecular structures were optimized at the MP2/6-31G\*\*++ level with the help of the *ab initio* package [GAMESS](#) (General Atomic and Molecular Electronic Structure System) [6]. The computations were performed on clusters of Linux PC machines at ENSTA. Geometry optimizations were performed for the following cations: MethylOxonium; EthylOxonium; 1-PropylOxonium, 2-PropylOxonium and 1-ButylOxonium, 2-ButylOxonium, IsoButylOxonium, TertButylOxonium. Vibrational frequencies and ZPEs are computed, and visual depictions of expected experimental IR spectra are simulated with the help of Lorentzian functions. MP2 Frequencies were not scaled. Curves are displayed with the help of the [Xgraphic](#) software [7].

With the help of the graphics package [MolDen](#), edition of Z-matrices and production of 2D images were performed [8].

Since static 2D images are not often providing an easy way to understand molecular structures, optimized geometries are also displayed ( see HTML version of this paper ) with the help of the freely available [ChemApp](#) Java applet [9] written by John and [George Purvis](#). This did not appear obvious to us when our graphics were first created during the summer of 1999, but the *CAChe* format is now linked to a proprietary product distributed by [Cache Software](#) [10], a Fujitsu subsidiary. Most regrettably, the original [ChemApp](#) internet page no longer exists. We have nevertheless preserved an almost complete copy of the original site that we have made available to our readers for convenience. This did not appear obvious to us when our graphics were first created during the summer of 1999, but the *CAChe* format is now linked to a proprietary product distributed by [Cache Software](#) [10], a Fujitsu subsidiary. Since the [ChemApp](#) applet [9] reads only files in the [CAChe](#) format [11], we used the

program [Babel](#) [12] (A Molecular Structure Information Interchange Hub ) to convert GAMESS outputs into *CAChe* files. There is now a Open Source successor to Babel : [OpenBabel](#) [13] . When the original [ChemApp](#) site was still online, Dr. [George Purvis](#) provided us a very kind help in order to diagnose a bug and find a way to avoid it. It is also interesting to notice that the *CAChe* format [11] allows also to display Molecular Orbitals This feature has not been used in this article.

The HTML version of this paper contains many pictures, data and supplementary material that could not be reasonably provided in a printer-ready PDF format.

### Determination of Initial Geometries

A first step is to determine initial reasonable geometries that are going to be included in the GAMESS input file, before starting energy computation and geometry optimization. We have used the geometry database server [CORINA](#) (COoRdINAtes) [14] that generates a set of atomic coordinates. In order to use [CORINA](#) [14] one should enter the description of the molecule using a [SMILES](#) ( Simplified Molecular Input Line Entry Specification ) string [15]. The [SMILES](#) [15] strings concerning alkyl-oxonium cations under study are listed below ( cf. Table 1).

**Table 1.** SMILES strings.

Name	Formulae	SMILES string
<b>MethylOxonium Cation</b>	$\text{CH}_3\text{-OH}_2^+$	<chem>C[OH2+]</chem>
<b>EthylOxonium Cation</b>	$\text{CH}_3\text{-CH}_2\text{-OH}_2^+$	<chem>CC[OH2+]</chem>
<b>1-PropylOxonium Cation</b>	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}_2^+$	<chem>CCC[OH2+]</chem>
<b>2-PropylOxonium Cation</b>	$\text{CH}_3\text{-CH(OH}_2^+)\text{-CH}_3$	<chem>C(C)(C)[OH2+]</chem>
<b>1-ButylOxonium Cation</b>	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}_2^+$	<chem>CCCC[OH2+]</chem>
<b>2-ButylOxonium Cation</b>	$\text{CH}_3\text{-CH(OH}_2^+)\text{-CH}_2\text{-CH}_3$	<chem>CC(CC)[OH2+]</chem>
<b>IsoButylOxonium Cation</b>	$(\text{CH}_3)_2\text{-CH-CH}_2\text{-OH}_2^+$	<chem>C(C)(C)C[OH2+]</chem>
<b>TertButylOxonium Cation</b>	$(\text{CH}_3)_3\text{-C-OH}_2^+$	<chem>C(C)(C)(C)[OH2+]</chem>

### Computations of Optimized Geometries

Concerning the **MethylOxonium Cation**, a symmetric  $C_s$  geometry seems a rather obvious choice. We nevertheless optimized with and without a  $C_s$  symmetry constraint, as expected the geometry and energy are the same. The vibronic energy is the sum of the electronic energy and the vibrational Zero-Point-Energy (ZPE), computed within the framework of the adiabatic approximation and the harmonic

approximation (cf. Table 2). The fact that the ZPE is very slightly lower in magnitude in the  $C_s$  geometry is just an artefact.

**Table 2.**

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)
$C_1$ CORINA	-115,693.616	-115.627,745
$C_s$ CORINA	-115,693.616	-115.627,746

Concerning the **EthylOxonium Cation**, we started from the structure proposed by [CORINA](#) which appears as a reasonable guess ( cf. Table 3 ). The ZPE is 0.094,880 Hartree.

**Table 3.**

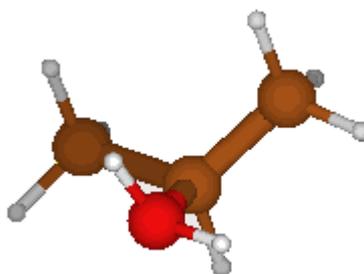
Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)
$C_1$ CORINA	-154.889,501	-154,794,621

Concerning the **1-PropylOxonium Cation**, we started from the structure proposed by [CORINA](#) without symmetry constraint. The ZPE is 0,124.270 Hartree. The initial and final geometries seem quite reasonable, and no other geometries were investigated ( cf. Table 4 ).

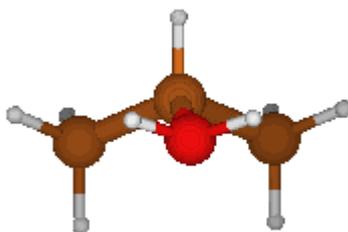
**Table 4.**

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)
$C_1$ CORINA	-194.074,869	-194.049,401

Concerning the **2-PropylOxonium Cation**, we started from the structure proposed by [CORINA](#) which is asymmetric (cf. Fig 1) . We tried yet another geometry (cf. Fig 2) where hydrogen atoms nearby the oxygen atoms are located respectively on each side of a symmetry plane ( cf. Table 5). This  $C_s$  structure features a lower energy. It appears that CORINA failed to guess the optimized geometry in this case.



**Figure 1.**  $C_1$  structure CORINA.



**Figure 2.**  $C_s$  structure.

**Table 5.**

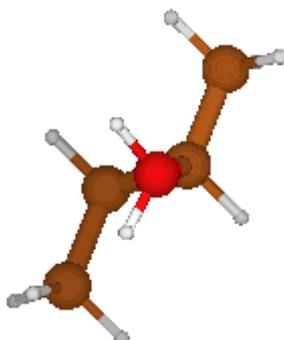
Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)
$C_1$ CORINA	-194,085.307	-193.962,213
$C_s$	-194,085.994	-193,962.813

**1-ButylOxonium Cation:** We kept the structure proposed by [CORINA](#). It seems difficult to envision any other reasonable candidate geometry. Trying to impose an overall  $C_s$  symmetry would require two pair of hydrogen atoms to face one another.

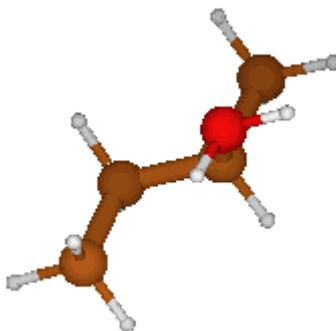
**Table 6.**

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)
$C_1$ CORINA	-233.259,678	-233.106,238

**2-ButylOxonium Cation:** We considered two types of geometries : the first one being proposed by [CORINA](#), the second one is obtained from the former geometry by a  $120^\circ$  rotation of the oxonium group. This latter geometry (nearly symmetric in the vicinity of the oxonium group) features a lower energy (cf. Table 7). It appears that CORINA again failed to guess the optimized geometry.



**Figure 3.**  $C_1$  structure CORINA.

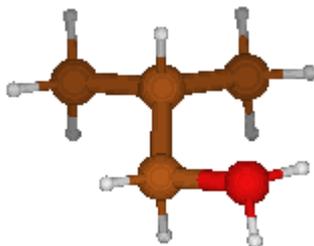


**Figure 4.** nearly  $C_s$  structure.

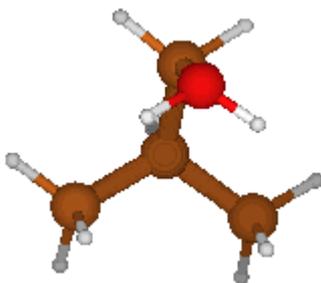
**Table 7.**

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)	Nature
$C_1$ CORINA	-233,271.199	-233,118.970	local minimum
nearly $C_s$	-233,271.777	-233,119.432	global minimum

**IsoButylOxonium Cation** : We considered four types of geometry. The first one is an asymmetric geometry proposed by [CORINA](#) ( cf Fig 5 ). Since this molecule, at a very first glance, could feature a symmetry plane, we explored also three other more symmetric  $C_s$  geometries, among which one ( cf Fig 6 type B) turned to be a local minimum. The geometry proposed by [CORINA](#) however prevailed as the best geometry for a global minimum (cf Table 8).



**Figure 5.**  $C_1$  CORINA.



**Figure 6.**  $C_s$  type B.

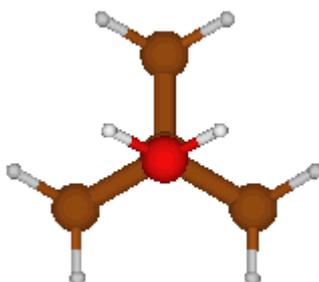
Table 8.

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)	Nature
C <sub>1</sub> CORINA	-233.263,333	-233.110,484	global minimum
C <sub>s</sub> type A	-233.255,232	-233.102,368	saddle point
C <sub>s</sub> type B	-233.262,854	-233.110,094	local minimum
C <sub>s</sub> type C	-233.260,681	-233.108,464	saddle point

**TertButylOxonium Cation** : [CORINA](#) suggested a very reasonable C<sub>s</sub> (cf Fig 7) symmetric structure. We also explored another C<sub>s</sub> symmetric structure which turned to be, as expected, a saddle point (cf. Table 9).

Table 9.

Symmetry	Electronic Energy (Hartree)	Vibronic Energy (Hartree)	Nature
C <sub>s</sub> CORINA	-233.282,026	-233.130,937	global minimum
C <sub>s</sub>	-233.280,442	-233.129,881	saddle point

Figure 7. C<sub>s</sub> global minimum.

Vibrational absorption spectra are also reported for each geometry under consideration and could provide some help to identify molecular geometries, for example the IsoButylOxonium global minimum (cf Fig. 8 ) and the TertButylOxonium global minimum (cf. Fig. 9). For more see the HTML version.

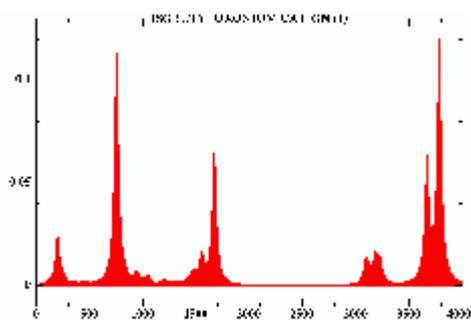
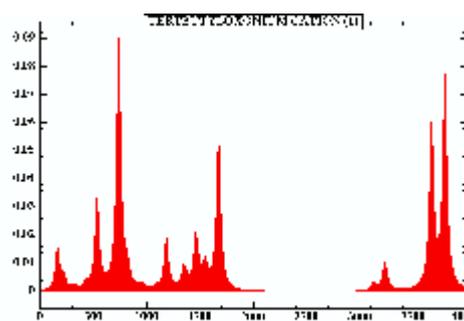
Figure 8. IsoButylOxonium (Y intensity au / X frequency cm<sup>-1</sup>).

Figure 9. TertButylOxonium.

## Discussion

Costly Hessian computations were achieved for three purposes : first to determine the topological nature of geometries on the Potential Energy Surface, second to take into account the ZPE, within the adiabatic and harmonic approximations, and third to compute the vibrational spectra.

We took care of including ZPE contributions in determining the lower geometry for each species. However, ZPE contributions did not modify the choice between stationary points that were under consideration, among possible candidates for the global minimum geometry. The lowest electronic energy geometry turned always to be the lowest vibronic energy. No dramatic isotopic substitution effects are therefore envisioned, at least in the gas phase.

The geometry predictions obtained from [CORINA](#) are, in general, validated by our MP2 computations. However, in the two cases of 2-PropylOxonium and 2-ButylOxonium, do [CORINA](#) predictions appear to be in disagreement with our *ab initio* computations. This corresponds to a 75% success rate.

The fact that that the IsoButylOxonium cation does not feature any symmetry is going to unfortunately imply more costly computations in order to estimate the electronic absorption spectrum of the corresponding radical.

Interactive techniques of geometry visualization, such as provided by the [ChemApp](#) Java applet allow to understand and investigate geometry structures in a much more convenient way than 2D static pictures. One big advantage of a Java applet is that it does not require the reader to have any helper application or plugin installed in her/his browser. However, many browsers have the Java compatibility disabled, and it take times to load the Java interpreter into memory. Once the [Java Virtual Machine](#) (JVM) is loaded, other visualizations are much quicker to appear.

Another aspect concerning visualization tools is that a freely available software does not necessarily means that it is a free software under the [GPL](#) [16] or an open source software. At the time, in 1999, when our decision was made, we were not conscious enough of the issues involved in the long term. There is no guarantee that a software that was freely available in 1999 will continue to be easily available or updated. This is a lesson that has been learned.

## Conclusion

We computed the lower energy geometries and infrared absorption spectra of the isolated small  $C_nH_{2n+1}OH_2^+$ ,  $n=1,2,3,4$  alkyl-oxonium cations : MethylOxonium, EthylOxonium, 1-PropylOxonium, 2-PropylOxonium, 1-ButylOxonium , 2-ButylOxonium , IsoButylOxonium and TertButylOxonium, while taking into account the ZPE.

The geometrical structures proposed by [CORINA](#) [14] appeared to be the correct guesses in six out of eight cases. The two prediction failures concern the 2-PropylOxonium and 2-ButylOxonium Cations.

Vibrational absorption spectra are also reported for each geometry under consideration.

The usefulness of a freely available Java Applet has been demonstrated in order to communicate research results concerning molecular structures. However, a freely available software is not necessarily a free software or an open source software.

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